Supplementary Information (SI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2025

Electronic Supplementary Information for

Lowering the bandgap of poly(diketopyrrolopyrrole-altterchalcogenophene)s via chalcogen effects for shortwave infrared phototransistors

Mei Rao,^a Ting Jiang,^b Pengfei Pang,^c Yang Han, ^{*a} Deyang Ji,^b Yunfeng Deng^a and Yanhou Geng^{*a,c}

^aSchool of Materials Science and Engineering and Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Key Laboratory of Organic Integrated Circuits, Ministry of Education, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.

^bInstitute of Molecular Aggregation Science, Tianjin Key Laboratory of Molecular Optoelectronic Science and Key Laboratory of Organic Integrated Circuits, Ministry of Education, Tianjin University, Tianjin, 300072, China.

^cJoint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou 350207, China E-mail: yang.han@tju.edu.cn; yanhou.geng@tju.edu.cn

Content:

1.	General procedures and instruments2
2.	Synthesis of monomers and polymers
3.	The fabrication and measurements of OTFT and OPT4
4.	Supplementary data6
5.	References

1. General procedures and instruments

¹H NMR spectra were measured on a Bruker 400-MHz spectrometer with acetone-d⁶ ((CD₃)₂CO) and chloroform-d (CDCl₃) as solvent at 25 °C. Elemental analysis was conducted on a Elementar Vario EL elemental analyser. Molecular weights and polydispersity indices of the polymers were determined by high temperature gel permeation chromatography (HT-GPC) on a PL-GPC 220 system at 150 °C with 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was conducted on a TG 209 F3Tarsus analyser at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Differential scanning calorimetry (DSC) scans were recorded on a TA DSC25 instrument at a heating/cooling rate of 10 °C min⁻¹ under a nitrogen flow. UV-vis-NIR absorption spectra of the polymers were recorded on a Shimadzu UV-3600Plus spectrometer. Solution absorption spectra were measured in o-dichlorobenzene (o-DCB) with a repeating unit concentration of 10⁻⁵ mol L⁻¹. The films for the absorption spectra measurements were prepared by spin-casting the o-DCB solutions on quartz substrates. With Bu₄NPF₆ (0.1 mol L⁻¹) as supporting electrolyte, film cyclic voltammograms (CV) were recorded in anhydrous CH₃CN on a CHI660a electrochemical analyser with a three-electrode cell at a 100 mV s⁻¹ scan rate. A glassy carbon electrode with 6 mm diameter, a Pt wire, and a saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. The in-plane and out-of-plane X-ray diffraction (XRD) of the films were measured by a Rigaku Smart Lab with Cu K_a source ($\lambda = 1.54056$ Å) in air with a power of 9 kW. Atomic force microscopy (AFM) measurements were conducted on a Bruker MultiMode 8 instrument in tapping mode.

All density functional theory (DFT) calculations were operated on a Gaussian 09 program.¹ The geometry optimization, the frontier molecular orbitals (FMOs) calculations and the scan potential relaxed potential energy surface scans of the polymers are calculated at B3LYP(D3) level of theory using the basis 6-31G(d,p) for C, H, O, N and S atoms, and the sdd basis for Se and Te atoms. All the side chains were simplified by methyl groups.

2. Synthesis of monomers and polymers

Unless otherwise noted, chemical reagents and solvents were purchased from commercial sources and used without further purification. Toluene and *N*, *N*-dimethyl formamide (DMF) were distilled using standard method prior to use. Compounds **2a** was purchased from commercial sources and compounds **1a**, **1b** and **2b** were prepared according to the literatures.²⁻³ All air and water sensitive reactions were carried out under nitrogen atmosphere, following the standard Schlenk technique.

Polymer ThDPP-Se: Into a Schlenk tube, **1a** (160.00 mg, 166.13 µmol), **2a** (77.38 mg, 169.45 µmol), Pd₂(dba)₃(4.56 mg, 4.98 µmol), PPh₃ (5.23 mg, 19.94 µmol), anhydrous toluene (7.50 mL) and anhydrous DMF (0.75 mL) were added in a glovebox. The reaction was stirred at 115 °C for 20 min. 2-Bromobenzene (0.5 mL) was added followed by stirring for another 12 h in dark. The mixture was cooled to room temperature and precipitated in methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with ethanol, acetone and hexane in succession. ThDPP-Se was obtained as a dark solid (150.56 mg) in a yield of 97%. GPC: $M_n = 65.6$ kDa, D = 3.0. Elemental Anal. Calcd for (C₅₄H₈₂N₂O₂S₂Se)_n (%) : C 69.42, H 8.85, N 3.00; Found: C 69.45, H 8.60, N 3.05.

Polymer ThDPP-Te: The polymer was obtained from **1a** (155.00 mg, 160.94 µmol) and **2b** (82.95 mg, 164.16 µmol) as a dark solid (150.29 mg) in a yield of 95% following the same procedure for the synthesis of ThDPP-Se. GPC: $M_n = 51.1$ kDa, D = 2.5. Elemental Anal. Calcd for (C₅₄H₈₂N₂O₂S₂Te)_n (%): C 66.53; H 8.57; N 2.77; Found: C 65.98, H 8.41, N 2.92.

Polymer SeDPP-Se: The polymer was obtained from **1b** (152.00 mg, 143.81 µmol) and **2a** (67.00 mg, 146.69 µmol) as a dark solid (140.46 mg) in a yield of 95% following the same procedure for the synthesis of ThDPP-Se. GPC: $M_n = 51.1$ kDa, D = 2.5. Elemental Anal. Calcd for $(C_{54}H_{82}N_2O_2Se_3)_n$ (%): C 63.08; H 8.04; N 2.72; Found: C 62.83, H 7.98, N 2.77.

Polymer SeDPP-Te: The polymer was obtained from **1b** (170.00 mg, 160.84 µmol) and **2b** (74.92 mg, 164.06 µmol) as a dark solid (155.44 mg) in a yield of 94% following the same procedure for the synthesis of ThDPP-Se. GPC: $M_n = 39.0$ kDa, D = 2.5. Elemental Anal. Calcd for (C₅₄H₈₂N₂O₂Se₂Te₃)_n (%): C 60.23; H 7.68; N 2.60; Found: C 60.04, H 7.62, N 2.60.



Scheme S1. Synthetic Route to the four polymers

3. The fabrication and measurements of OTFT and OPT

Top-gate and bottom-contact OTFT devices were fabricated on 1.5 cm × 1.5 cm highly doped silicon wafers with 300 nm SiO₂ layer. The substrates were cleaned with deionized water, acetone and isopropanol in an ultrasonic cleaner and dried under a nitrogen flow, following by heating at 120 °C for 10 min to remove the solvent. Subsequently, 30 nm Au source/drain electrodes was patterned on the substrates by vacuum-evaporation. The channel length (L) and channel width (W) are 80 μ m and 5.6 mm, respectively. Subsequently the substrates were treated with UV-ozone for 5 min. Then the semiconductor films were deposited by spin-coating 4.0 mg mL⁻¹ polymer *o*-DCB solutions at 2000 rpm for 120 s in glove box, followed by annealing at 120 °C for 10 min. Subsequently, CYTOP (Asahi Glass, type CTL-809M) with a thickness of about 900 nm was spin coated at 2000 rpm for 2 min as dielectric layer, and annealed at 100 °C for 40 min. Finally, 80 nm Al as gate electrode was vacuum-evaporated on the top of semiconductor layer.

For devices with bottom gate and top contact geometry, highly doped Si wafers covered with 300 nm SiO₂ layer were used as substrates. The substrates were cleaned following the above procedure. After treating with UV-ozone for 10 min, the Si wafers was immersed in dodecyltrichlorosilane (OTS-12) solution in anhydrous toluene (1/1000, v/v) at 60 °C for 1h. Then the Si wafers were cleaned by toluene and isopropanol. Then the semiconductor films were deposited by spin-coating 4.0 mg mL⁻¹ 1,1,2,2-tetrachloroethane (TCE) solutions of polymers at 2000 rpm for 120 s in glove box and annealed at 250 °C for 10 min. For the mixed solution of SeDPP-Te and PC₆₁BM, PC₆₁BM was first dissolved in TCE with a concentration of 4 mg mL⁻¹ and was add to the SeDPP-Te solution to keep the concentration of SeDPP-Te at 4 mg/mL. The mixture was stirred in 100 °C overnight and the films were prepared as the above method. Lastly, Au source and drain electrodes were deposited by vacuum evaporation.

All OTFT devices were measured under ambient conditions using Keysight B1500A analyser. Filed-effect mobility values in saturation regime were calculated according to equation:

$$\mu = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}} \right)^2$$

where L/W is the channel length/width, I_{DS} is the drain-source current, μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer, V_{GS} are the gate voltage.

The phototransistor performance of the polymers was measure under the light source of adjustable illumination power NIR LED with a wavelength of 1030 nm. The light power density was corrected by Thorlab PM100D with a Si photodetector. According to the transfer curves of the devices in dark and 1030 nm light illumination, the photoresponsivity (R), the photosensitivity (P), and specific detectivity (D^*) were calculated according to following equation:

$$R = \frac{I_{ph}}{P_{opt}} = \frac{I_{light} - I_{dark}}{P_{int}A}$$

$$P = \frac{I_{ph}}{I_{dark}} = \frac{I_{light} - I_{dark}}{I_{dark}}$$

$$D^* = \frac{RA^{1/2}}{(2qI_{dark})^{1/2}}$$

where I_{light} is the drain-source current under 1030 nm light illumination, I_{dark} is the drainsource current in the dark, I_{ph} is the difference between I_{light} and I_{dark} , A is the light illumination area of the polymers, P_{opt} and P_{int} are the incident light intensity and incident light power density, q is the charge of an electron.

4. Supplementary data



Figure S1. TGA (a) and DSC (b) curves of polymers in N_2 atmosphere at a heating/cooling rate of 10 °C min⁻¹.



Figure S2. Temperature-dependent solution UV-vis-NIR absorption spectra of the polymers in o-DCB with a repeating unit concentration of 10⁻⁵ mol L⁻¹.



Figure S3. The film cyclic voltammograms of the polymers and $PC_{61}BM$.



Figure S4. The side views of methyl substituted trimers (a), the (FMO) distribution diagrams and energy levels of methyl substituted trimers of the ThDPP-Se (b) and SeDPP-Se (c) calculated by DFT.



Figure S5. The chemical structure (a), the relaxed potential energy (E) surface scans (b) and the bond length plots (c) of the polymers.

-	Po	lymers	SAMs	$\mu_{ m h}(m cm^2V)$	⁷⁻¹ s ⁻¹)	$I_{\rm on}/I_{\rm off}$	$V_{\mathrm{th}}\left(\mathrm{V} ight)$	
-	ThI	OPP-Se	OTS-18	0.63±0.15	5(0.77)	10 ⁵ to 10 ⁶	3 to 10	
	Thl	OPP-Se	OTS-12	0.73±0.14	(0.77)	10^{5} to 10^{7}	3 to 11	
	SeI	OPP-Se	OTS-18	0.57±0.09	0(0.66)	10^4 to 10^5	7 to 15	
	SeI	OPP-Se	OTS-12	0.38±0.06	(0.42)	10^{5} to 10^{7}	-1 to 8	
Polym	lumor	Device	$\mu_{ m h,a}$	$_{ m vg}\left(\mu_{ m h,max} ight)$	<i>I</i> / <i>I</i> (b)	V_{T}	Annealing	Temperature
1 Olyli	Geometry		$[cm^2 V^{-1} s^{-1}]^{(a)}$		I on / I off	[V] ^(c)	((°C)
		TGBC	4.00±	=0.45 (4.50)	10^3 to 10^5	-7 to -1		120
ThDPP	P-Se	TGBC	3.42±	=0.73 (4.23)	10^3 to 10^5	-15 to -21		250
		BGTC	0.71±	=0.12 (0.80)	10^5 to 10^6	17 to 26		120
		BGTC	0.73±	:0.14 (0.77)	10^5 to 10^7	3 to 11	,	250
	ThDPP-Te	TGBC	2.86±	=0.35 (3.15)	10 ³ to 10 ⁶	-11 to -20		120
ThDPP		TGBC	1.42	±0.43(1.80)	10^3 to 10^6	-16 to -22	,	250
		BGTC	0.53±	20.05 (0.54)	10^3 to 10^4	20 to 30		120
		BGTC	0.78±	20.14 (0.87)	10^5 to 10^7	3 to 12	,	250
	SeDPP-Se	TGBC	1.57±	:0.18 (1.77)	10^2 to 10^4	-10 to -17		120
SeDPP		TGBC	1.12	±0.18(1.34)	105	-15 to -21		250
56011		BGTC	0.32±	20.06 (0.34)	105	15 to 24		120
		BGTC	0.38±	=0.06 (0.42)	10^5 to 10^7	-1 to 8		250
	SeDPP-Te	TGBC	1.99±	0.45 (2.46)	10^2 to 10^5	-9 to -2		120
Senpp		TGBC	1.47	±0.15(1.64)	10^3 to 10^4	-22 to -27	,	250
50011		BGTC	0.58±	=0.03 (0.61)	10^5 to 10^6	10 to 21		120
		BGTC	0.64±	=0.08 (0.72)	10^3 to 10^4	10 to 16	,	250

 Table S1. OTFT performance of polymers with different self-assembled monolayers (SAMs).



Table S2. OTFT performance of polymers under different annealing temperatures.

Figure S6. Typical transfer curves of TGBC devices annealed at 120 °C and 250 °C.



Figure S7. Typical transfer curves of BGTC devices annealed at 120 °C and 250 °C.



Figure S8. Typical transfer(a-d) and output (e-f) characteristics of TGBC OTFT devices based on ThDPP-Se (a,e), SeDPP-Se (c,g) and BGTC OTFT devices based on ThDPP-Se (b,f) and SeDPP-Se (d,h).



Figure S9. The absorption spectra of SeDPP-Te film and SeDPP-Te blending film with 20% mol $PC_{61}BM$.

Polymer	condition	R_{max} (A/W)	P_{max}	D^*_{\max} (×10 ¹⁰ Jones)
SeDPP-Te	0%PC ₆₁ BM	6.65±1.71 (7.50)	1.27±0.37 (2.03)	3.36±1.08 (5.08)

 Table S3. The phototransistor performance of SeDPP-Te.



Figure S10. Transfer curves evolution of pure SeDPP-Te film under dark and upon illumination by light of 1030 nm.

Polymer	condition	$\mu_{\rm h}({\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$I_{ m on}/I_{ m off}$	$V_{ m th}\left({ m V} ight)$
SeDPP-Te	0%PC ₆₁ BM	0.64±0.08 (0.72)	10^5 to 10^6	10 to 21
SeDPP-Te	10%PC ₆₁ BM	0.56±0.10 (0.66)	10^{6} to 10^{7}	3 to 7
SeDPP-Te	20%PC ₆₁ BM	0.53±0.16(0.69)	10^{6} to 10^{7}	2 to 7
SeDPP-Te	40%PC ₆₁ BM	0.42±0.14 (0.59)	10 ⁵ to 10 ⁶	-5 to 0
SeDPP-Te	60%PC ₆₁ BM	0.64±0.07 (0.71)	10^5 to 10^6	0 to 6
SeDPP-Te SeDPP-Te	40%PC ₆₁ BM 60%PC ₆₁ BM	0.33±0.10(0.09) 0.42±0.14 (0.59) 0.64±0.07 (0.71)	10 ⁵ to 10 ⁶ 10 ⁵ to 10 ⁶	-5 to 0 0 to 6





Figure S11. Typical transfer (a-d) and output (e-f) characteristics of BGTC OTFT devices based on SeDPP-Te with 10 mol% $PC_{61}BM$ (a,e), 20 mol% $PC_{61}BM$ (b,f) 40 mol% $PC_{61}BM$ (c,g) and 60 mol% $PC_{61}BM$ (d,h).



Figure S12. Transfer curves of SeDPP-Te with 10% $PC_{61}BM$ (a), SeDPP-Te with 40% $PC_{61}BM$ (b) and SeDPP-Te with 60% $PC_{61}BM$ (c) upon illumination by light of 1030 nm.

Table S5. The phototransistor performance of SeDPP-Te with PC₆₁BM.

Polymer	condition	R_{max} (A/W)	P _{max}	$D_{\max}^*(\times 10^{11} \text{ Jones})$
SeDPP-Te	10%PC ₆₁ BM	27.76±1.32 (29.03)	34.08±6.61 (47.42)	1.62±0.17 (1.84)
SeDPP-Te	20%PC ₆₁ BM	30.96±2.78 (34.92)	25.73±2.67 (30.97)	2.30±0.25 (2.76)
SeDPP-Te	40%PC ₆₁ BM	30.30±2.33 (32.99)	22.07±4.38 (28.15)	1.66±0.22 (1.96)
SeDPP-Te	60%PC ₆₁ BM	20.58±1.97 (21.73)	3.47±1.34 (6.32)	1.26±0.14 (1.47)



Figure S13. The calculated photosensitivity (a), detectivity D* (b) of phototransistors based on SeDPP-Te with 20 mol% $PC_{61}BM$ under 1030 nm illumination at different V_G , and (c) the plot of photocurrent against time after illumination for the calculation of photoconductive gain parameter.



Figure S14. Out-of-plane (a) and in-plane (b) XRD profiles of thermally annealed SeDPP-Te: $PC_{61}BM$ blends, the films were deposited on bare Si/SiO₂ substrates by drop casting. Thermal annealing was conducted at 250 °C for 10 min under N₂ atmosphere.



Figure S15. AFM height (top) and phase (bottom) images $(2 \ \mu m \times 2 \ \mu m)$ of SeDPP-Te: PC₆₁BM blends films with 10 mol% (a), 20 mol% (b), 40 mol% (c) and 60 mol% (d) PC₆₁BM. The films were deposited on OTS-modified Si/SiO₂ substrates by spin coating. Thermal annealing was conducted at 250 °C for 10 min under N₂ atmosphere

Polymer	condition	stacking dis	tance [Å]	coherence	coherence length (L_c)		
1 01 1 1101	Condition	Lamellar(d100)	π-π (d100)	Lamellar(d100)	π-π (d100)		
ThDPP-Se	-	21.3	3.72	140.0	73.3		
ThDPP-Te	-	21.0	3.82	151.1	90.7		
SeDPP-Se	-	21.4	3.70	97.4	67.9		
SeDPP-Te	-	20.8	3.76	150.6	79.7		
SeDPP-Te	10%PC ₆₁ BM	20.7	3.77	152.7	63.6		
SeDPP-Te	20%PC ₆₁ BM	20.9	3.76	158.2	65.0		
SeDPP-Te	40%PC ₆₁ BM	20.9	3.76	164.0	63.3		
SeDPP-Te	60%PC ₆₁ BM	20.9	3.75	170.8	52.0		

Table S6 The packing distances and lamellar stacking coherence lengths of polymer films



Figure S16. The GPC curves of ThDPP-Se (a), ThDPP-Te (b), SeDPP-Se (c) and SeDPP-Te (d).



Figure S17. ¹ H NMR spectrum of 1a (400 MHz, CDCl₃, 25 °C).



Figure S18. ¹ H NMR spectrum of 1b (400 MHz, CDCl₃, 25 °C).



Figure S19. ¹ H NMR spectrum of 2b (400 MHz, (CD3)₂CO₂, 25 °C).

5. References

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, S11 D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

- [2] Z. Wang, Y. Shi, Y. Deng, Y. Han, Y. Geng, Adv. Funct. Mater., 2021, 31, 2104881.
- [3] C. Stephens, D. Sweat, Synthesis, 2009, 19, 3214.